Excess Oxygen of Chromia, I

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Chromia hydrogel precipitated by the urea method and dried in air at 25°C (25) has little or no excess oxygen beyond Cr_2O_3. Dried at 85°C (85), it has about 125 meq/mole Cr and 135 has 400–500. Removal of the excess oxygen by hydrogen at 300°C gives an amorphous, microporous material designated A–Cr(III). Heating 25 to 300°C *in vacuo* or in flowing helium gives a nearly identical A–Cr(III) and both can be heated to nearly 500°C *in vacuo* or in helium without crystallization.

The excess oxygen of 85 and 135 is unavailable to I^- aq in heterogeneous iodometry. Activation *in vacuo* to progressively higher temperatures develops availability to I^- aq and, after activation to about 350°C, almost all excess oxygen of 135 reacts with I^- aq. Activation to still higher temperatures leads to crystallization to mesoporous α-Cr_2O_3 (probably by the fluxing action of Cr(VI)) with loss of about 70% of the area, 85 crystallizes at somewhat higher temperatures. By 450°C, both have about 2.8 atoms of Cr(VI) per nm^2. At 300°C, hydrogen converts them to X–Cr(III), the crystalline analog of A–Cr(III).

Oxygen adsorbed on A–Cr(III) at −78°C (probably as $Cr(IV)O_2^-$) is completely available to I^- aq, behaves as a 4-e oxidant and is reduced by hydrogen at 140°C. Adsorption of oxygen at 100°C is more complicated. Chromia with adsorbed oxygen crystallizes upon heating *in vacuo* at 400°C.

INTRODUCTION

Chromia (in this paper, meaning the amorphous hydrous oxide prepared by treating Cr^{3+} aq with base and materials derived therefrom by heating) is a catalyst for a number of reactions, in particular, for oxidation of carbon monoxide and hydrocarbons (*1*), for dehydrocyclization of heptane to toluene (*2*), for hydrogenation of ethylene even at −78°C (*3–5*), and for isotopic exchange between hydrocarbons and deuterium (*4,6,7*). The existence of these reactions and the isotopic simplicity of the last reaction and of the previous reaction using deuterium have led to considerable mechanistic interest in chromia as a catalyst.

Preparation of chromia catalysts involves precipitation of a hydrous gel which is washed and dried in the oven usually at about 100°C (*4,6*). This material becomes a catalyst for reactions between hydrocarbons and hydrogen or deuterium only after activation to above 300°C. The drying and activation processes involve loss of water and it was proposed (*6,7*) that some of the loss results from condensation of surface OH^- to generate Cr^{3+}(cus) and O^{2-}(cus) pairs where (cus) means *coordinatively unsaturated surface*. The chemisorption capacities at −78° for carbon monoxide and for oxygen are almost identical and they rise with the temperature of activation, first becoming detectable at about 200°C (*6*). It was concluded that the sites which chemisorb carbon monoxide and oxygen are Cr^{3+}(cus). It has been proposed that Cu^{3+}(cus), O^{2-}(cus) pair sites are the catalytic sites of several reactions involving hydrogen and hydrocarbons (*6*).

It has long been known that chromia takes up oxygen upon exposure to air above 100°C and acquires oxidizing capac-

ity, to be called here *excess oxygen* (*3*). The term implies nothing about whether the oxidizing species are oxygen with an oxidation number greater than −2 or chromium with an oxidation number greater than +3 or both. Because of such excess oxygen, it has been customary during activation first to heat chromia in hydrogen to about 300°C. Activation to higher temperatures is continued *in vacuo* or in flowing helium or hydrogen (*4,6*). The problem then arises as to whether Cr^{3+}(cus) may be generated, at least in part, consequent to reduction of oxidized surface by hydrogen.

Of previous studies of the oxidation of chromia, those of Weller and Voltz (*3*) and of Deren and Haber (*8*) are most applicable. Weller and Voltz studied samples of chromia which had been converted to α-Cr_2O_3 of a surface area of 35 m²/g by cycling several times between oxygen and hydrogen at 350 or 500°C. They studied the oxygen and hydrogen consumption during the cycling, they showed that the excess oxygen could be measured iodometrically, and they found that the catalytic activity for low temperature hydrogen–deuterium exchange and for the hydrogenation of ethylene at −78°C was much greater in the reduced than in the oxidized state. Deren and Haber iodometrically determined the amount of excess oxygen in

chromia as a function of the temperature of heating in oxygen. The amount increased with the temperature of heating from 100° to about 350°C and then decreased as the chromia crystallized to α-Cr_2O_3. Some excess oxygen could be extracted by water as chromate. This quantity was very small for heating at 100°C but became large for 350°C.

We endeavor in this paper further to elucidate the details of the introduction of excess oxygen into chromia during its drying or as a result of the adsorption of oxygen on activated chromia, the nature of excess oxygen, its removal, and its effect upon the conversion of amorphous chromia to α-Cr_2O_3. The following paper reports the reactions of diphenylpicrylhydrazine and diphenylpicrylhydrazyl with various chromias and with chromia/silica gels.

Chromia presents a complicated system. It occurs with various water contents, as amorphous or crystalline, mesoporous or microporous, with various surface concentrations of Cr^{3+}(cus) and O^{2-}(cus), and with no excess oxygen or with various kinds of excess oxygen. To facilitate discussion, the types of chromia important in the present work and symbols for them are listed in Table 1. Figure 1 is a summary of many of the reactions which interconvert the various chromias and it will provide a
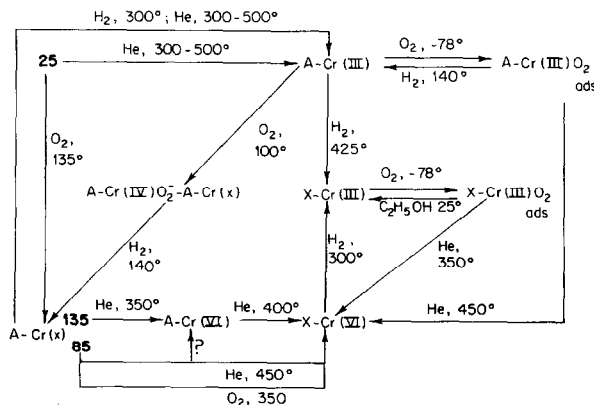

FIG. 1. Scheme for the interconversion of the various types of chromia.

TABLE 1

CLASSIFICATION OF CHROMIAS

	Amorphous, microporous	Crystalline, mesoporous
No excess oxygen	A–Cr(III)	X–Cr(III)
Excess oxygen as surface Cr(VI)	A–Cr(VI)	X–Cr(VI)
Oxygen adsorbed on A– or X–Cr(III)	A–Cr(III)O$_2$ads	X–Cr(III)O$_2$ads
Inaccessible excess oxygen	A–Cr(x)	–

framework for the discussion section of this paper.

EXPERIMENTAL

Unless otherwise specified, the samples of chromia used in these papers started as hydrogels prepared by the urea method (9) in which a solution of chromium nitrate and urea is simmered at about 90°C. Ammonia, which is liberated uniformly throughout the solution, serves as the base and carbon dioxide bubbles from the solution. This bubbling serves to keep the solution relatively free from oxygen, a fact which, as will be seen, may have some consequences.

Hydrogel dried in the oven at 85°C for three weeks is designated **85**. This material further dried for 12 hr at 135°C is designated **135**. Some **85**, washed several times in doubly distilled water and then dried at 135°C for 12 hr, is listed as **85W135**. Several samples, designated **25**, represented hydrogel which has been dried at 25°C in a desiccator by G. J. Antos and E. L. Blackman. The operation required several months. Usually, 60–80 mesh material was used.

The code showing the conditions of treatment subsequent to drying is exemplified by **85, H$_2$300, He450**. Here, a sample of **85** was heated in flowing hydrogen at a temperature rising to 300°C and held at that temperature for 6–12 hr. The hydrogen was replaced by helium and the temperature increased to 450°C at which temperature there was a hold for 6–12 hr. Other hold periods than 6–12 hr

are shown as follows: **85, H$_2$300, He450, O$_2$25(0.1)** where the terminal (0.1) is the period in hours.

Iodometric analyses for oxidizing capacity were run in a 200 cm^3 bulb to the top of which was attached a glass stopcock and to the bottom of which was attached a closed-end section of 16 mm tubing 20 cm long. About 0.5 g of chromia placed at the bottom of the 16 mm tubing gave a layer only 2–3 mm thick. The iodometric apparatus was connected to the vacuum line by a Swagelock union with Teflon ferrules and evacuated with a mercury vapor diffusion pump trapped with liquid nitrogen. Except with the solution technique, the sample was then activated *in vacuo* and, when desired, treated with various gases. In the solution technique used with samples dried between 25 and 135°C, 10 cm^3 of concentrated hydrochloric acid was placed in a funnel attached above the stopcock and deaerated by a stream of argon before admission to the apparatus. Heating for several hours at 60–80°C was required for dissolution of samples of **135**. A deaerated solution of about 5 g of potassium iodide in 50 cm of water was then added. Much of the oxidizing capacity appeared to be in the gas phase probably as chlorine. After shaking for twenty min, the 16 mm tubing was cracked and the contents of the apparatus rapidly poured into a flask containing sodium bicarbonate. The solution was then back-titrated with a solution of sodium thiosulfate to the starch end point.

Samples of chromia which had been

heated much above 135°C were not dissolved by concentrated hydrochloric acid. In these cases, 50 cm^3 of 0.5 M sulfuric acid was added instead. Otherwise the procedure was the same. Here, the chromia was not dissolved, the reactions proceeded in a heterogeneous system, and shaking was for 12 hr.

The presence of air leads to slow oxidation of the acidic iodide solution. For example, deliberate addition of 10 cm^3 of air to the apparatus in the absence of added chromia led to the reduction of 6–10% of the oxygen. In a run on **85**, in which there was an air leak, twice the normal oxidizing capacity was found. However, since reaction of oxygen is slow, were free oxygen to be released during dissolution of unactivated samples containing excess oxygen, a low oxidizing capacity would be found. In an experiment on **85**, the gas phase was examined for the presence of oxygen gas chromatographically. None was found.

Oxidizing capacity arising from retained nitrate. Chromia hydrogel prepared by the urea method retains ammonium nitrate, carbon dioxide and perhaps a little urea (6). Values of %N in the dried gel determined by conventional microanalysis are given in Table 2. The %C was about 1.3

except it was 0.3 for **85W135**. The low values of %C and %N for **85W135** accord with the previous observation (10) that washing the dried gel removes much of the contaminants.

Since we found NO_3^- to be a three electron oxidizing agent in our iodometry, the 25 mmole N/mole Cr of **85** if all present as nitrate could contribute an oxidizing capacity of 75 meq/mole Cr. In no other case could retained ammonium nitrate contribute an important fraction of the total oxidizing titer. We doubt that ammonium nitrate contributes much to the oxidizing titer of activated **85**. The ammonium nitrate of chromia decomposes at 200–250°C largely to nitrogen and nitrous oxide (6); various samples of **25** activated to 300–400°C exhibited small or zero titer; a sample of chromia prepared by the urea method from chromium chloride behaved very much like that from the nitrate and dried at 25°C its oxidizing titer was 0, at 125°C, 360 meq/mole Cr.

DISCUSSION

Excess oxygen vs temperature of drying. As shown in Table 2, samples of chromia dried in air at about 25°C are nearly devoid of the capacity to oxidize iodide ion.

TABLE 2

IODOMETRIC ANALYSES OF CHROMIA SAMPLES

Chromia	Oxidizing capacity meq/mole Cr	Formula	%N[a]
25	0	Cr_2O_3	0.0
25[b]	2	Cr_2O_3	0.4–0.5
85	127	$Cr_2O_{3.13}$	0.8–0.9
25,135[c]	424	$Cr_2O_{3.42}$	0.4–0.5
135	470	$Cr_2O_{3.47}$	0.8–0.9
85W135	500	$Cr_2O_{3.50}$	0.0
85,air285(14)[d]	328	$Cr_2O_{3.33}$	
85,air310(14)[d]	1000	$Cr_2O_{4.00}$	

[a] %N on basis of anhydrous Cr_2O_3. Microanalysis by Miss H. Beck on an F and M Carbon–Hydrogen–Nitrogen Analyzer, Model 185.

[b] Two other samples of **25** gave larger values but well below those of **85**.

[c] A sample of the second **25** dried subsequently at 135°C.

[d] Samples of **85** heated statically in air at 285 and 310°C for 14 hr. Analysis was by the heterogeneous technique. The total excess oxygen may not have been titrated.

Oxidizing capacity appears upon drying at 85°C. At 135°C the capacity corresponds about to $Cr_2O_{3.5}$, a value near those reported by Deren and Haber (8) and Carruthers, Fenerty and Sing (11).

A–Cr(III) (upper left of Fig. 1). Dried below 100°C, chromia has a water content very roughly corresponding to $Cr_2O_3 \cdot 5H_2O$ and it is amorphous to x-rays. During heating *in vacuo* or in flowing gas, water is lost rather rapidly between 100 and 200°C. If the heating is in hydrogen, by 300°C, the formula is approximately $Cr_2O_3 \cdot 1/2H_2O$ and much of this water of constitution is present as surface hydroxyl groups. The chromia is still amorphous, of high area [about 250 m^2/g (6,12)], and devoid of excess oxygen, i.e., it is A–Cr(III), Table 1. Essentially indistinguishable A–Cr(III) result from **25**, vac300 and **25**, He300. All A–Cr(III) remain amorphous during further heating to above 450°C in helium, nitrogen or *in vacuo*, Table 3. These materials are microporous and almost devoid of mesopores as shown in Fig. 2 [see also (12,13)]. The
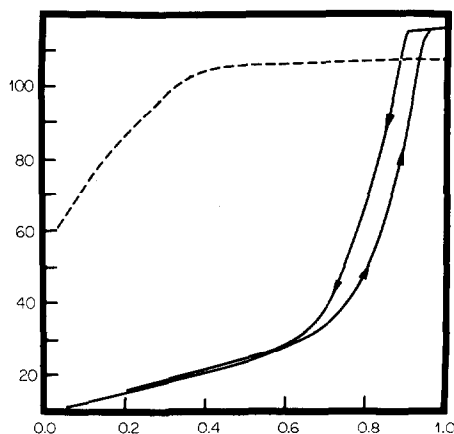

FIG. 2. Nitrogen physisorption isotherms at the temperature of liquid nitrogen determined on an Aminco Adsorptomat. Full line: **85W135**, He430 of Table 2. Dashed line: **85W135**, H_2304, He423 of Table 2. Desorption exhibited no hysteresis to $p/p_o = 0.2$ for the latter sample. y-axis, cm^3 N_2 adsorbed (STP)/g; x-axis, relative pressure.

procedures just described permit one to prepare a series of microporous A–Cr(III) in which the water content decreases and the content in Cr^{3+}(cus) and O^{2-}(cus) increases with increasing temperature of ac-

TABLE 3
ANALYSES FOR CRYSTALLINITY AND TEXTURE

Sample	X-Ray diffraction	A_s m^2/g^a	Isotherm type	Av. pore radius, Å	Pore vol, cm^3/g
85W135,He430	α-$Cr_2O_3{}^b$	61	mesoporous	60	0.19
85W135,$H_2$304,He423	amorphous^c	320	microporous	5^d	0.17
85W135,$H_2$304, He423,O_2-78,He450	α-Cr_2O_3	57	mesoporous	60	0.14
85,He450	α-Cr_2O_3	90	mesoporous	40	0.14
25,vac440 air25(0.1),vac280	amorphous	230	microporous	5^d	0.12
85W135,H_2O(23mm) 340,air25(0.2) vac340(0.5)	CrOOH^e	24	$-^f$	large	?

^{a} Specific surface area per gram of fully dehydrated chromia.

^{b} Also α-Cr_2O_3: **85W135**,vac430 and **25** impregnated with H_2CrO_4aq,vac425.

^{c} Also amorphous: **25**,He350,He430 and **25**,vac450.

^{d} From the *t*-plot of de Boer and Lippens, see also Ref. (12).

^{e} Orthorhombic CrOOH, see A. N. Christensen, *Inorg. Chem.* **5**, 1452 (1966).

^{f} BET type II, rising rapidly against $p/p°$ greater than 0.82, no sign of pore filling. The oxidizing capacity of gels treated with water vapor appears to be lower than those activated *in vacuo*, for example **85W135** activated in H_2O at 306° gave 90 meq/mole Cr.

tivation. **25, H₂300** and **100, H₂300** had the same catalytic behavior in the hydrogenation of 1-hexene (6) and we do not think that the reduction of excess oxygen in the latter case led to much if any difference from **25, H₂300**. However, the matter has not been investigated in detail from the catalytic point of view and no catalytic data are available on **135, H₂300**.

A–Cr(III) is known as a non-microporous aerogel which is converted into microporous A–Cr(III) by compression (*12*).

X–Cr(VI) (bottom of Fig. 1). As has long been known, chromia is converted to crystalline α-Cr₂O₃ when heated in air to somewhat above 300°C. It has been suggested that (a) crystallization is triggered by the heat of oxidation of chromia (*11,13*), (b) it results from the formation of bound CrO₃ which acts as a flux (6). We now find that, when chromia containing almost any kind of excess oxygen is heated to about 400°C in flowing helium or *in vacuo*, it crystallizes to an α-Cr₂O₃ covered with a layer of surface "chromate" (see Table 3 and the following paper). Even oxygen adsorbed on A–Cr(III) at −78°C is effective. Thus, the mere presence of higher oxidation states of chromium is sufficient as the following treatments, all of which give X–Cr(VI), exemplify: **85W135,He430, 85,He450, 85W135,H₂304,He423,O₂-78(0.1),He450, 25** impregnated with CrO₃aq and heated *in vacuo* at 425°C, as well as **85, O₂350**.

During crystallization, the surface area falls, the pores enlarge but the pore volume changes little. The product is mesoporous (Fig. 2). It appears that the larger the quantity of excess oxygen, the lower the temperature of crystallization, the larger the pore diameter, and the smaller the area (Table 3).

X-Cr(III) (center of Fig. 1) can be prepared in two ways: reduction of the "chromate" on X-Cr(VI) with hydrogen at about 300°C, for example, **85, He450,**

H₂300, and treatment of A–Cr(III) with hydrogen at about 425°C, for example **85, H₂425**. The textures of both are essentially the same as that of **85, He450** in Table 3. Since crystallization by hydrogen at 425°C probably results from the fluxing action of small amounts of Cr(II) (*12*), **85, H₂425** may contain small quantities of surface Cr(II) but we believe that **85, He450, H₂300** does not.

These high area samples of α-Cr₂O₃ are, of course, microcrystalline and we do not know the exact degree of conversion of amorphous to crystalline. The X-Cr(III) made by A–Cr(III), **H₂425** has been considered to be "microcrystalline α-Cr₂O₃ supported on amorphous chromia" (*14*).

Crystalline hydrates of Cr₂O₃ have been reported to result from exposure of chromia to water vapor (*13*), see the last run of Table 3.

A–Cr(III)O₂ads and *X–Cr(III)O₂ads* (right of Fig. 1). The irreversible chemisorption of oxygen on chromia at −78°C measures the content in Cr³⁺(cus) as 0.2 molecules of oxygen/nm² for **100, H₂260, He260** and 1.0 for **100, H₂300, He410** (7). Values so determined are compared with those from heterogeneous iodometry in Table 4, runs 1, 2, 4, and 5. It is assumed that O₂ads behaves as a four electron oxidizing agent. Agreement is good. Therefore, adsorbed oxygen is not desorbed by exposure to dilute sulfuric acid, it acts as a four electron oxidizing agent, and it is accessible to the iodide ion despite its location in micropores only 1 nm in diameter.

An example of X–Cr(III)O₂ads is provided by run 7. Similar examples in the following paper gave larger titers.

Exposure to oxygen at 25°C yields larger oxidizing titers than exposure at −78°C as was also true for oxygen chemisorption (6). Pretreatment with water vapor or ammonia largely eliminates Cr³⁺(cus) and blocks reaction with oxygen as shown by runs 13 and 14 of Table 4. Adsorbed at −78°, carbon dioxide blocks the adsorption

TABLE 4

ADSORPTION OF OXYGEN ON ACTIVATED CHROMIA

Run	Sample[a]	Oxidizing capacity meq/mole Cr	$4(O_2ads)$[b]
1	25,vac372,O_2-78	89	100
2	25,vac456,O_2-78	107	130
3	25,vac430,O_2-78,vac440	71	(60)[c]
4	85,vac300,$H_2$300,vac425,O_2-78	99	120
5	85,vac300,$H_2$300(2),vac480,O_2-78	104	140
6	135,vac402,$H_2$460,$O_2$25,vac425	48	(55)[c,d]
7	25,vac482,$H_2$482,O_2-78	18	55
8	25,vac460,O_2(1.2 atm)25(0.1)	177	(140)[d]
9	25,vac383,O_2(1.8 atm)100	228	(100)[d]
10	85,vac286,$H_2$330(2),vac415, O_2(1.4 atm)103,vac25	145	(120)[d]
11	85,vac330,$H_2$330(2.5),vac450, N_2O(1.2 atm)25	9	
12	25,vac455,N_2O(1.2 atm)25,vac420	3	
13	85,vac285,$H_2$320,vac416, H_2O(vap)25,vac25,$O_2$25	10	
14	25,vac390,$NH_3$25(0.25),$O_2$25	0	
15	25,vac430,O_2-78,$H_2$140	0	
16	85,$H_2$330,vac420,$O_2$105,$H_2$140	47	

[a] Adsorption of oxygen at $-78°C$ was for 5 min and was followed by evacuation at $-78°C$.

[b] Four times the amount of oxygen chemisorbed at $-78°C$ estimated from Ref. (6). About 12% of this oxygen is desorbed upon warming to $25°C$ and would have been pumped off in the present experiments before iodometry.

[c] Estimated for adsorption at $-78°C$ without subsequent evacuation at high temperatures.

[d] Estimated for adsorptions at $-78°C$. Adsorption at higher temperatures should be larger.

of oxygen at $-78°C$, but adsorbed at $25°C$ it blocked only 80% of the adsorption of oxygen observed in its absence. Neither benzene vapor nor propane at $25°C$ affected the adsorption of oxygen at $25°C$. The heat of adsorption of oxygen at $25°C$ on activated A–Cr(III) caused the sample to get hot and the temperature considerably to exceed the listed $25°C$. The samples of runs 13 and 14 got hot upon exposure to water vapor and ammonia but not upon the subsequent exposure to oxygen.

Exposure to oxygen at $100°C$ gave still larger titers (run 9). This was also true of the extent of oxygen chemisorption (6). Some chromic acid was extracted during the iodometry of such products unlike the case for chromias treated with oxygen at $-78°C$.

$A–Cr(x) \rightarrow A–Cr(VI) \rightarrow X–Cr(VI)$ (bottom of Fig. 1). Samples of 85 and the 135's show by heterogeneous iodometry little of the oxidizing titer exhibited in solution iodometry (Table 2 and Fig. 3). Samples of the 135's develop oxidizing titer for heterogeneous iodometry upon heating *in vacuo*. After activation at $225°C$, they give a titer which is about 20% that shown by solution iodometry of the initial chromia and at $350°C$, nearly 100% (Fig. 3). Traces of chromic acid are extracted from the initial 135's, larger amounts after activation at $225°C$ and very large amounts after activation at $350°C$. This last product, designated A–Cr(VI), consists of amorphous chromia with large amounts of surface Cr(VI). There must be a gradual transition between the initial 135, designated A–Cr(x), and A–Cr(VI).
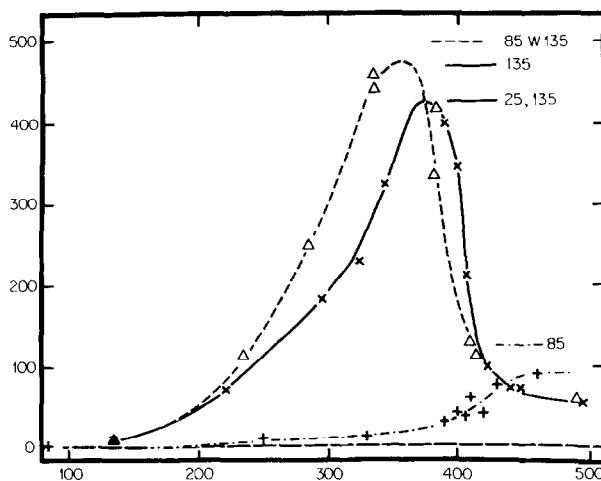
FIG. 3. Iodometric titer meq/mole Cr of chromias of different initial drying temperatures as a function of the temperature of activation *in vacuo*. The heterogeneous iodometric technique was used. The horizontal lines at the right of the figure represent the iodometric titer of the unactivated samples by the solution technique. The X's represent both 135 and 25,135 since data from these two samples both fell on the full black line, y-axis, temperature of activation in °C; x-axis, meq/mole Cr.

Heating A–Cr(VI) to still higher temperatures gives X–Cr(VI) whose surface content in Cr(VI) appeared to level off at about 450°C to 2.8 atoms of Cr(VI)/nm². The large loss in oxidizing capacity which accompanies crystallization must be accompanied by the liberation of gaseous oxygen.

Presumably A–Cr(III)O₂ads becomes converted to A–Cr(VI) at some temperature below that of crystallization to X–Cr(VI).

85 contains about one-quarter as much excess oxygen as the 135's. Its oxidizing titer by heterogeneous iodometry rises more slowly with increasing temperature than that of the 135's and does not pass through a maximum. Substantial chromic acid is extractable only after activation beyond 400°C. A–Cr(VI) is formed from 85 at higher temperatures than from the 135's. The temperature of formation of X–Cr(VI) is also higher and the specific area is larger than that formed from 135. However, the content per square nanometer in surface Cr(VI) is the same as that formed from the 135's (Fig. 3 and Table 3).

X–Cr(VI) and A–Cr(VI) are low in

(cus) sites. Exposure to oxygen at 25°C does not result in warming nor does it lead to an increase in the oxidizing titer. Presumably Cr³⁺ ions just below the surface are coordinated with oxygen atoms shared with Cr(VI) to form surface "chromic chromate."

Reduction of excess oxygen. Excess oxygen is removed from A–Cr(x) by flowing hydrogen at 300°C in 2 hr but the reaction is rather slow. Pulses of hydrogen about 6 sec wide in a stream of very pure helium were passed through a small bed of 85 in an apparatus of Dr. Beverley I. Brookes. No detectable consumption of hydrogen was observed at 325°C. At 450°C, the first pulse was fully consumed but, after several pulses, no further loss of hydrogen occurred. The total consumption of hydrogen was equivalent to about 60 meq/mole Cr.

Oxygen chemisorbed on A–Cr(III) at −78°C is more reactive and is eliminated by flowing hydrogen at 140°C as shown by run 15, Table 4 [see also Ref. (6)]. However, A–Cr(III) treated with oxygen at 100°C is more resistant to reduction at 140°C. Some but not all excess oxygen is reduced (run 10 vs 16 in Table 4).

X–Cr(VI) is largely reduced by exposure to ethanol or acetone for a few min at 25°C but exposure to carbon monoxide, ammonia or benzene does not change the oxidizing titer to within the experimental scatter. Oxidation of isopropyl alcohol by chromia/alumina has been reported to occur at 30°C (15). X–Cr(VI) is reduced by diphenylpicrylhydrazine at 25°C as reported in the following paper.

The nature of excess oxygen. We have suggested that oxygen reacts at −78°C with the Cr^{3+}(cus) on A–Cr(III) to form surface $Cr(IV)O_2^-$ (6). Cr(VI) cannot have been formed because A–Cr(III)O_2ads does not release chromic acid when treated with dilute acid and because it is reduced by hydrogen at 140°C whereas A–Cr(x) and A–Cr(VI) are not. $Cr(IV)O_2^-$ must be stable thermally at 140°C but as mentioned earlier it must react at higher temperatures to form A–Cr(VI).

From a detailed examination by infrared spectroscopy, Zecchina and co-workers (16) concluded that oxygen was dissociatively adsorbed at 25°C on highly dehydroxylated X–Cr(III) in a form best represented as Cr=O. Presumably, the chromium here would be Cr(V). Upon heating at 200–400°C, Cr=O reacts to form surface "chromate-like" species. The ratio of coverages by carbon monoxide and oxygen on our X–Cr(III) was substantially greater than unity (6) and this led us to suggest that oxygen is adsorbed on X–Cr(III) as peroxide ions bridging two Cr^{3+}(cus), a form which from a coverage point of view would be equivalent to Cr=O. In the present work, our examination of X–Cr(III)O_2ads was cursory and we have no reason to disagree with the conclusions of Zecchina. On amorphous chromia, however, carbon monoxide coverages are the same as those of oxygen (6) and most Cr^{3+}(cus) are probably isolated. Thus we tentatively retain the conclusion that oxygen is adsorbed on A–Cr(III) as $Cr(IV)O_2^-$.

The Turin group (17) also found that

nitrous oxide reacts with X–Cr(III) to generate surface Cr=O although to a lesser extent than does oxygen. Nitrous oxide generated only a small oxidizing titer from our X–Cr(III) (Table 4, runs 11 and 12). However, the Turin group also noted that surface oxidation by nitrous oxide was favored by a highly dehydroxylated surface and our X–Cr(III), having been formed at lower temperatures, should have been less dehydroxylated than theirs.

Precipitated hydrous chromia acquires excess oxygen when heated in air and in amount which increases with temperature rather rapidly in the interval 85–135°C (Table 2). We consider that this excess oxygen is formed in one or perhaps both of the following ways. (a) Oxygen reacts to form bulk Cr(IV) and/or Cr(V). It may be noted that CrOOH is rather readily oxidized to CrO_2 at higher temperatures (18–20). (b) Oxygen reacts to form Cr(VI) or perhaps Cr(IV) and/or Cr(V) located in pores too small to permit extraction of H_2CrO_4 or to permit entrance of I^- and egress of I_2. If (a) is correct, on heating, chromium atoms of intermediate oxidation states migrate to the surface (perhaps by electron transfer) and disproportionate to Cr(III) and Cr(VI). If (b) is correct, the higher oxidation states become accessible because of pore enlargement which occurs on heating. An argument against (b) is that A–Cr(III)O_2ads is reduced by I^- and, therefore, I^- can get in and I_2 out. However, in our experiments, the lowest temperature of activation of A–Cr(III) before adsorption of oxygen at −78°C was 372°C at which temperature the micropores are somewhat larger than after activation at lower temperatures [Ref. (6, p. 23)]. We also observed visually that A–Cr(III)O_2ads and **85W135**, vac250 took several hr for reduction by I^- whereas reduction of X–Cr(VI) was complete in a few min.

In any case one would expect the larger lattice energy of α-Cr_2O_3 vs that of amorphous chromia to inhibit insertion of chro-

mium ions of other oxidation numbers into its lattice and, therefore, the absence of an X–Cr(x) from Table 1 is not surprising.

The product of reaction at 100°C of activated A–Cr(III) with oxygen has the properties of both $Cr(IV)O_2^-$ and A–Cr(x). Only some of its oxidizing titer is removed by treatment with hydrogen at 140°C and the amount so removed is about that which would be expected from A–Cr(III)O_2ads. If, as appears likely, the residual excess oxygen resembles that in **85** and **135**, our earlier suggestion (6) that formation of $Cr(IV)O_2^-$ facilitates the oxidation of neighboring Cr^{3+} may be incorrect. The residual excess oxygen is sufficient to cause crystallization upon heating *in vacuo* to 420°. Thus, **25** vac406, $O_2$116, $H_2$140, vac444 gave an iodometric titer of 76 meq/mole Cr. During the last heating, oxygen gas was observed to be formed between 390 and 420°C in an amount equivalent to 51 meq/mole Cr. No more was formed upon further heating to 444°C.

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